Supporting Information for

$Na_2Fe(C_2O_4)F_2$: A new iron-based polyoxyanion cathode for Li/Na ion batteries

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1 Table S1 Unit cell information and atomic coordinates and BVS for metal atoms in $Na_2Fe(C_2O_4)F_2$

Atom	Wyck.	Site	x/a	y/b	z/c	Uequiv[Å^2]	BVS
Fe1	8f	1	0.17403(2)	0.16083(5)	0.21291(2)	0.00717(14)	2.022
Na1	8f	1	0.29790(6)	0.00423(16)	0.51447(8)	0.0121(2)	1.104
Na2	8f	1	0.06659(6)	-0.03217(16)	0.40099(9)	0.0116(2)	1.022
F1	8f	1	0.18763(9)	0.1500(2)	0.06049(11)	0.01252(3)	
F2	8f	1	0.17823(9)	0.1726(2)	0.37587(11)	0.01175(3)	
O1	8f	1	-0.05003(10)	0.5774(3)	0.10778(14)	0.00857(3)	
O2	8f	1	0.31304(10)	0.0289(3)	0.28934(13)	0.00644(3)	
O3	8f	1	0.39911(12)	0.3347(3)	0.31129(17)	0.01257(4)	
O4	8f	1	0.0364(1)	0.2707(3)	0.13864(14)	0.00855(3)	
C1	8f	1	0.38838(15)	0.1302(4)	0.31611(19)	0.00981(4)	
C2	8f	1	0.02406(15)	0.4791(4)	0.13964(18)	0.01041(4)	

2 Table S2 Selected bond lengths in $Na_2Fe(C_2O_4)F_2$

Atom1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Fe1	F1	1.9633(15)	Na2	F2	2.2624(18)
	F2	1.9782(15)		F1	2.2791(14)
	O4	2.1268(15)		O1	2.340(2)
	O2	2.1907(15)		O4	2.3587(19)
	O2	2.2051(18)		O3	2.586(2)
	O3	2.2255(18)	C1	O3	1.235(3)
Na1	F1	2.2253(14)		O2	1.266(3)
	F2	2.2543(19)		C2	1.570(3)
	O1	2.2987(17)	C2	O1	1.237(3)
	F2	2.2994(16)		O4	1.258(3)
	F1	2.3490(16)		C1	1.570(3)

3 Coordination polyhedra in $Na_2Fe(C_2O_4)F_2$

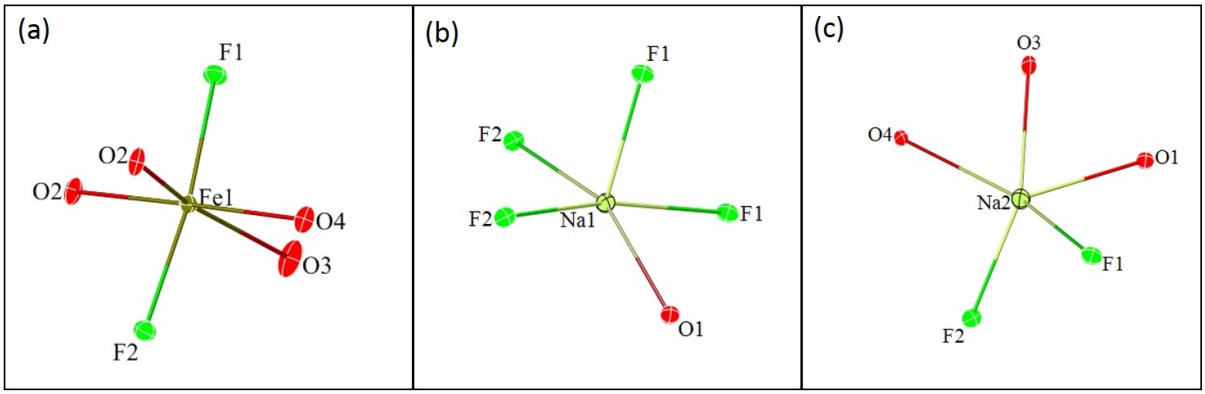

Figure S1 (a) FeO_4F_2 (b) $NaOF_4$ (c) NaO_3F_2

4 Morphology characterization of hand ground $Na_2Fe(C_2O_4)F_2$ powder sample

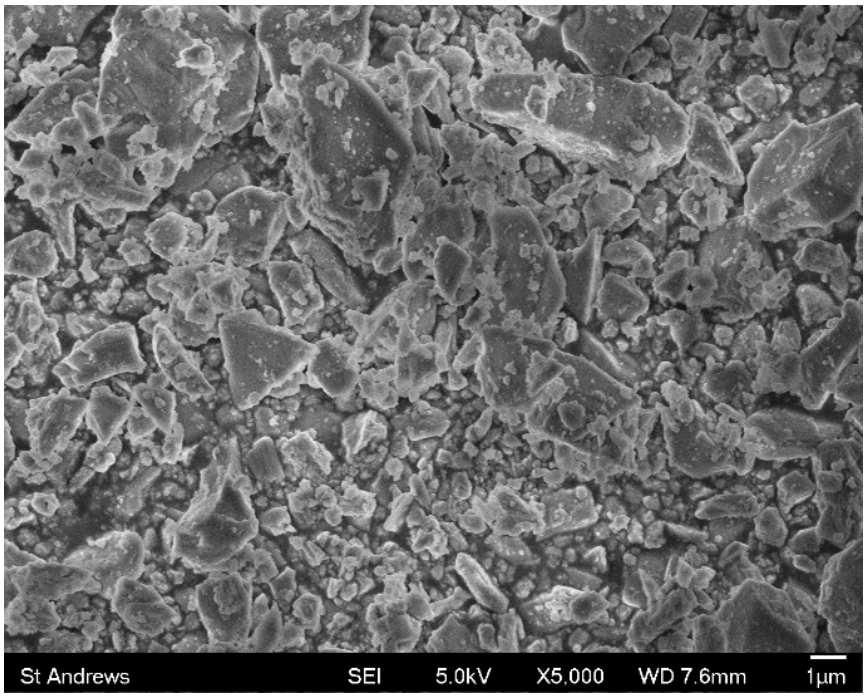

Figure S2 SEM image of hand ground $Na_2Fe(C_2O_4)F_2$ powder

5 UV-Vis Absorption Spectrum for $Na_2Fe(C_2O_4)F_2$ powder

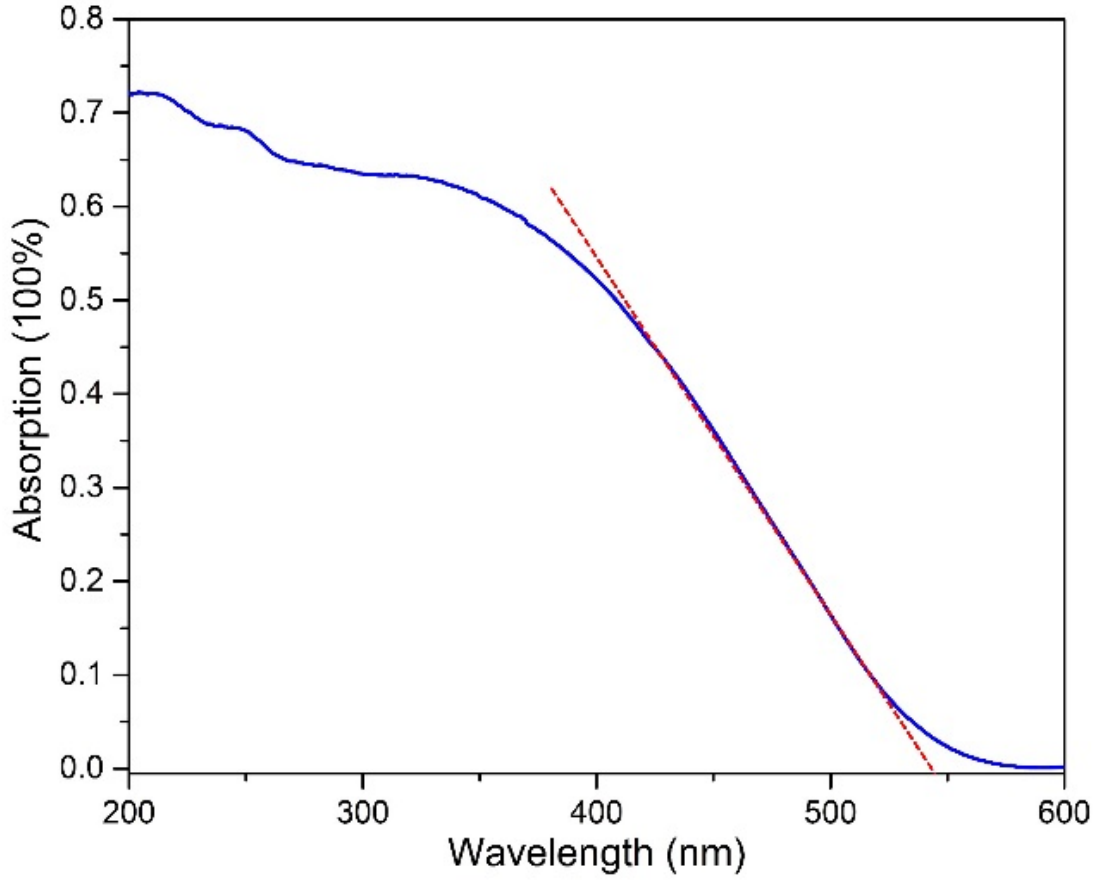

Figure S3 UV-Vis Absorption spectrum for $Na_2Fe(C_2O_4)F_2$ powder.

6 dQ/dV curve of initial charge/discharge profiles in LIB

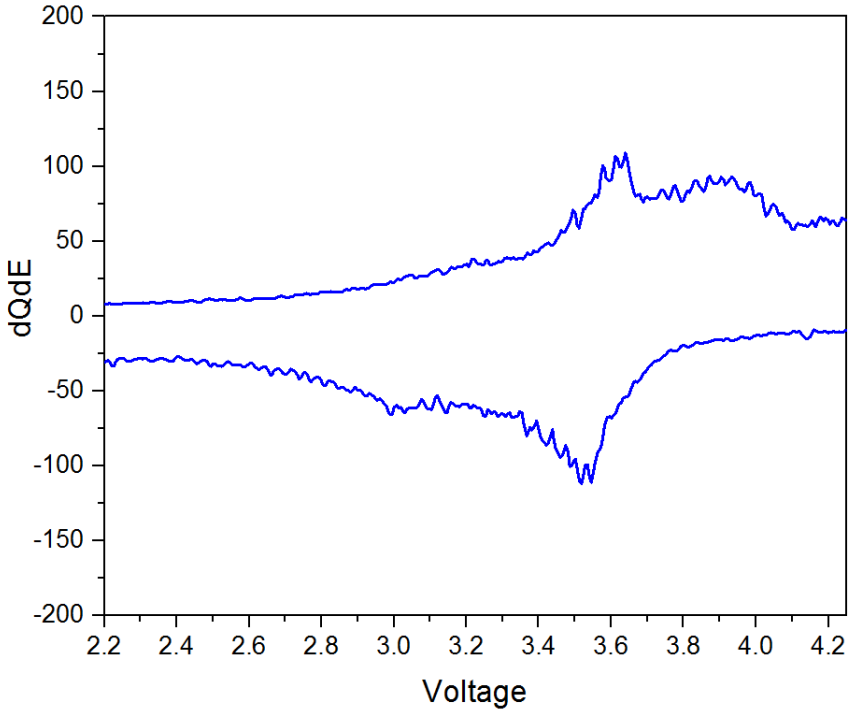

Figure S4 dQ/dV curve of initial charge/discharge profile in LIB

7 Table S3 Mössbauer parameters for $Na_2Fe(C_2O_4)F_2$ at different states corresponding to Figure 4d-f.

spectrum	*Comp.*	*IS mm/s*	*QS mm/s*	*LW mm/s*	*Abs %*	*Attribution*
Pure (Figure 4d)	Green-$Na_2Fe(C_2O_4)F_2$	1.23	2.56	0.28	91	Fe^{2+}
	Blue-[†]	1.22	1.58	0.63	9	Fe^{2+}
4.3 V-Charged (Figure 4e)	Green- $Na_2Fe(C_2O_4)F_2$	1.08	2.16	0.31	2	Fe^{2+}
	Blue-	1.24	2.76	0.27	8	Fe^{2+}
	Red-$NaFe(C_2O_4)F_2$	0.41	0.55	0.55	82	Fe^{3+}
	Pink-$NaFe(C_2O_4)F_2$	0.43	1.62	0.27	8	Fe^{3+}
2.0 V-Discharged (Figure 4f)	Green-$Na_2Fe(C_2O_4)F_2$	1.23	2.57	0.26	69	Fe^{2+}
	Blue-	1.20	1.93	0.45	5	Fe^{2+}
	Red-$NaFe(C_2O_4)F_2$	0.42	0.57	0.64	26	Fe^{3+}

[†]The blue line in the pristine sample indicates a minor environment, also in Fe(II) (high spin) but with slightly different parameters. It suggests a contribution arising from some defects in the bulk material, very small particles and/or amorphous material, or could be an impurity, such as amorphous $Fe(C_2O_4)\cdot 2H_2O$.

8 IR Spectroscopy of $Na_2Fe(C_2O_4)F_2$.

The absorption peaks in the IR spectrum are assigned as:

- 434 cm^{-1}: Fe-F antisymmetric stretching;
- 503 cm^{-1}: Fe-O symmetric stretching in the $[FeO_4]$ plane;
- 783 cm^{-1}: δ(OCO) bending modes;
- 902 cm^{-1}: ν(C-C) stretching vibration;
- 1309 cm^{-1}: ν_s(COO) involving dangling oxygen;
- 1456 cm^{-1}: ν_s(COO);
- 1606 cm^{-1}: ν_{as}(COO) involving dangling oxygen;
- 1674 cm^{-1}: ν_{as}(COO).

9 Solubility Analysis

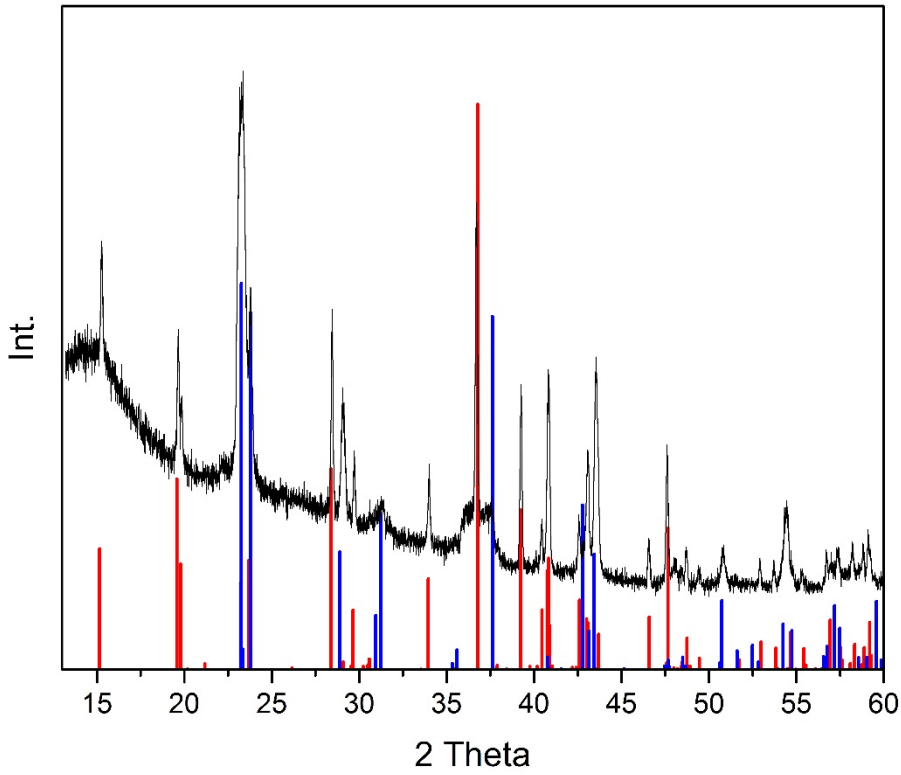

Figure S5. PXRD of left-over sample from $Na_2Fe(C_2O_4)F_2$ immersed in water for five days. Red: $Na_2Fe(C_2O_4)F_2$, Blue: $Fe(C_2O_4)\cdot 2H_2O$

10 Analysis of left-over sample from $Na_2Fe(C_2O_4)F_2$ immersed in 1M LiBr in CH_3CN

(a) EDX analysis

Spectrum processing:

Peak possibly omitted: 1.500 keV
Processing option: All elements analyzed (Normalised)
Number of iterations = 7

Standard:
C $CaCO_3$ 1-Jun-1999 12:00 AM
O SiO_2 1-Jun-1999 12:00 AM
F MgF_2 1-Jun-1999 12:00 AM
Fe Fe 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	6.98	10.94
O K	11.84	13.94
F K	72.96	72.35
Fe K	8.23	2.78
Totals	100.00	

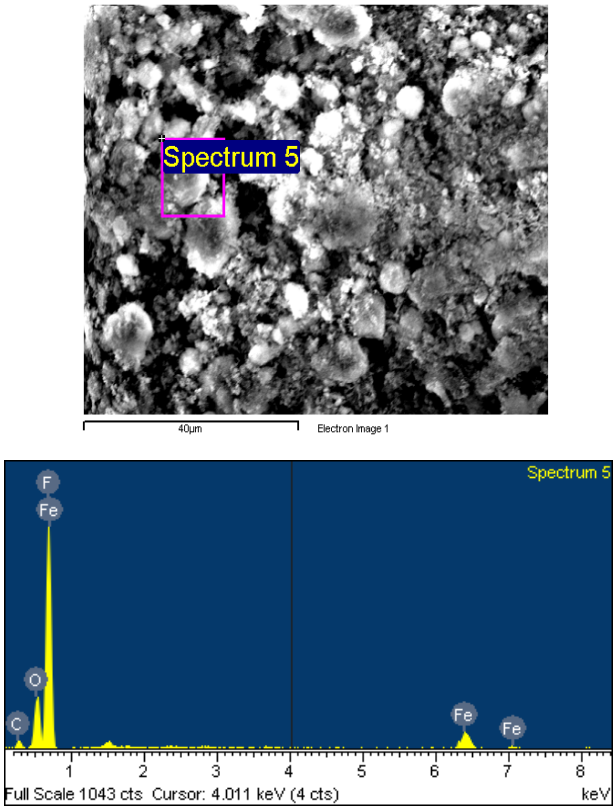

Figure S6. (a) SEM image and EDX spectrum

(b) PXRD analysis

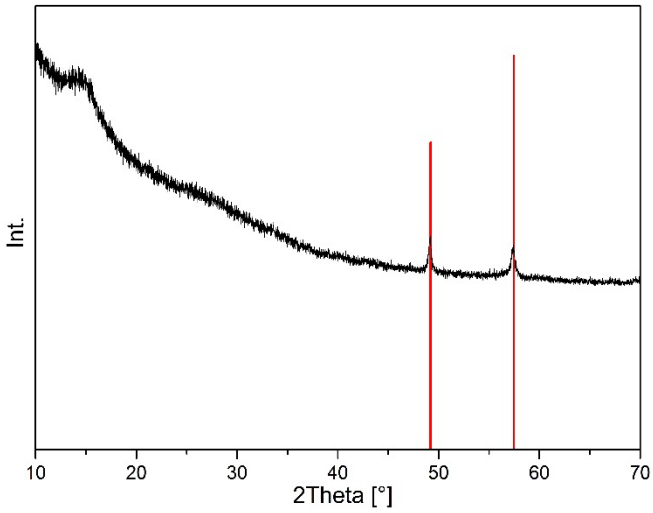

Figure S6. (b) PXRD of left-over sample